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## (54) TRANSPARENT HIGH-DENSITY POLYETHYLENE FILM AND PROCESS FOR ITS PRODUCTION.

(57) A 10- to 200  $\mu\text{m}$ -thick, transparent high-density polyethylene film of 0.935  $\text{g}/\text{cm}^3$  more in density having a haze value of less than 10%. It has a surface roughness of 0.001 to 0.15  $\mu\text{m}$ , a C-axis orientation function ( $F_c$ ) within the film of 0.10 to 0.50, and a difference in refractive index  $\Delta n$  between the amorphous portion and the crystalline portion within the film of 0.1000 to 0.1070. This film is produced by passing raw film through three heating rolls, i.e. a first heating roll ( $R_1$ ), a second heating roll ( $R_2$ ), and a third heating roll ( $R_3$ ) which are so heated that the temperature of  $R_2$  is higher than that of  $R_1$  and  $R_3$ , and that the temperature of  $R_2$  is not higher than the m.p. of the film and not lower than 105°C, and cooling the film. The film thus obtained has an excellent transparency, well-balanced strength in a machine direction and a transverse direction, remarkably large impact strength, and high Young's modulus, and is suited for use as wrapping film for containers of cigarettes, caramels, chocolates and confectionery such as chewing gum or candy.

DESCRIPTION

TECHNICAL FIELD

5 The present invention relates to a high density polyethylene type film with a remarkably superior transparency and a process for production thereof, more particularly, it relates to a transparent high density polyethylene type film with a good balance of strength  
10 in the M (machine) direction and T (transverse) direction, a remarkably high impact strength of the film, and a large Young's modulus, and a process for production thereof.

The present invention further relates to a high  
15 density polyethylene type film having a high strength, superior transparency, and good heat sealability, and a process for production thereof.

BACKGROUND ART

In the past, to obtain a high density polyethylene  
20 (hereinafter referred to as "HDPE") transparent film, the general practice has been to pass a molten resin through a slit die and cool it rapidly by chill rolls or water. However, with this method, to improve the formability, use has been made of resins with low  
25 molecular weights. Therefore, the transparent film obtained has had a relatively weak strength.

To obtain a strong film through the use of high molecular weight HDPE in forming a film, the general practice has been to use air-cooled inflation. With  
30 this method, it has been possible to obtain a film with superior strength through balancing the molecular orientation with the blow ratio, but since air is used for the cooling, only translucent or semitransparent films have been obtainable.

35 Attempts have been made to achieve a certain degree

of transparency (haze of about 15%) even with high molecular weight HDPE by passing the film through heated rolls having a surface gloss, so as to enhance the surface smoothness, but a transparency of a haze of 10% or less has not been obtained.

To make an HDPE film transparent, it is known to uniaxially draw a semitransparent HDPE film to a ratio of 5 to 10 and press it between rolls. The film obtained by this method does indeed have a superior transparency, but features a remarkable orientation in the drawing direction or rolling direction, and thus there is remarkable directionality in the aspect of film strength, resulting in a tendency to easy tearing, the obtaining of an insufficient strength, an uneven heat contraction, warping in the film, heat sealing inability, and other defects.

In the past, to obtain a high strength film from an HDPE film, the primary practice has been to use the inflation process. In inflation forming to obtain a high density film, as disclosed in Japanese Examined Patent Publication (Kokoku) No. 56-5172 and Japanese Unexamined Patent Publication (Kokai) No. 60-15122, it has been necessary to obtain a balance in the longitudinal and lateral orientation.

That is, if the orientation in the longitudinal direction is too great, longitudinal tearing easily occurs and if the orientation in the lateral direction is too great, a high strength film can not be obtained. Therefore, in general, in inflation forming, consideration is given to the ratio of the inflation ratio of the bubble and the diameter of the die, i.e., the blow ratio, the take up speed, and the frost line height. However, although it has been possible to impart strength to a film with a balance in the longitudinal and lateral orientations, in the case of a high density polyethylene, the transparency is poor, and thus the applications are limited at the present stage.

To improve the transparency of high density polyethylene type film, several other methods have been proposed.

For example, Japanese Unexamined Patent Publication  
5 (Kokai) No. 53-31768 proposes the technique of passing  
an original material thermoplastic resin film between a  
pair of rollers set to a clearance smaller than the  
thickness of the film and having a surface roughness of  
0.5  $\mu$  or less, at a temperature lower than the melting  
10 point or the softening point of the film, or lower, for  
rolling to obtain a film having a thickness smaller than  
the thickness of the original material film and a  
transparency of a haze of 4% or less. This technique is  
particularly characterized by the point of a maximum  
15 improvement of the surface state of the rolls used for  
the transparency treatment and, thereby, an improvement  
of the external haze, a factor governing the haze of  
film, to obtain a film with a superior transparency and  
gloss. However, by only defining the surface roughness  
20 of the rolls, improving the surface state of the rolls  
and, simultaneously, in this treatment, making the  
temperature lower than the melting point or the softening  
point of the film, or lower, and passing the film  
through the clearance between a pair of rolls, there are  
25 limits to the transparency of the HDPE film that can be  
obtained. In actuality, in this invention, examples  
relating to HDPE film were deleted from the embodiments  
in the subsequent examination process.

On the other hand, Japanese Unexamined Patent  
30 Publication (Kokai) No. 59-5032, proposes a technique  
for treating by pressure an HDPE inflation original film  
between smooth surfaces under a constant temperature to  
improve the optical characteristics of the obtained  
film. However, this technique, like the above-mentioned  
35 technique, obtains a film with improved optical characteristics through an improvement of only one of the  
factors governing the haze of the film, i.e., the

external haze, as shown by the statement in the publication that it was discovered at that time that the extent of the haze of the film and the extent of the insufficiency of the transparency were primarily due to the surface characteristics of the film. In the publication, there is a description of treating under pressure the original film between two or more opposingly positioned rollers and heating it under a constant temperature so as to facilitate the plastic deformation of the film, but there is no specific disclosure of heat treatment by the rolls. The embodiments only make specific mention of a method for placing the original film between two smooth sheets and using the contact with the sheet surfaces to flatten the original film.

#### DISCLOSURE OF THE INVENTION

The object of the present invention IS TO eliminate these problems in the prior art and to provide a transparent HDPE type film which is highly transparent, has a good balance in the film M direction and T direction, has a large film impact strength, has a high Young's modulus, and has excellent heat sealability, and a process for the production thereof.

Other objects and novel features of the present invention will become clear from the disclosure of the overall description.

According to the present invention, there is provided a 10 to 200  $\mu\text{m}$  thick film comprised of high density polyethylene having a density of  $0.935 \text{ g/cm}^3$  or more, this high density polyethylene type film having a film surface roughness of 0.001 to 0.15  $\mu\text{m}$ , preferably 0.002 to 0.15  $\mu\text{m}$ , more preferably 0.005 to 0.15  $\mu\text{m}$ , a coefficient of C axis orientation of the crystals in the film (Fe) of 0.10 to 0.50, preferably 0.10 to 0.40, more preferably 0.10 to 0.30, a difference  $\Delta n$  of the birefringence of the amorphous portions and crystalline portions in the film of 0.1000 to 0.1070, preferably 0.1000 to 0.1065, more preferably 0.1005 to 0.1060, and

a transparency of a haze of less than 10%, preferably less than 8%.

According to the present invention, there is further provided a 10 to 200  $\mu\text{m}$  thick film comprised of 5 50% by weight or more of high density polyethylene having a density of  $0.935 \text{ g/cm}^3$  or more and high pressure low density polyethylene having a density of  $0.910$  to  $0.930 \text{ g/cm}^3$  or straight chain low density 10 polyethylene having a density of  $0.880$  to  $0.930 \text{ g/cm}^3$ , this high density polyethylene type film having a film surface roughness of  $0.001$  to  $0.17 \text{ }\mu\text{m}$ , preferably  $0.001$  to  $0.15 \text{ }\mu\text{m}$ , more preferably  $0.010$  to  $0.15 \text{ }\mu\text{m}$ , a coefficient of C axis orientation of the crystals in the film (Fc) of  $-0.3$  to  $+0.50$ , preferably  $-0.2$  to  $0.40$ , 15 more preferably  $-0.2$  to  $0.30$ , a difference  $\Delta n$  of the birefringence of the amorphous portions and crystalline portions in the film of  $0.1000$  to  $0.1070$ , preferably  $0.1000$  to  $0.1065$ , more preferably  $0.1005$  to  $0.1060$ , and a transparency of a haze of less than 10%, preferably 20 less than 8%. Note that the amount of the above-mentioned high pressure low density polyethylene or straight chain low density polyethylene is preferably 1 to 50 parts by weight, particularly suitably 1 to 30 parts by weight.

25 Below, an explanation will be made of the case of use of three of these heating rolls.

The present inventors engaged in in-depth studies of techniques for making a high density polyethylene transparent, whereupon they learned that, although it is 30 necessary in the transparency treatment to pass the original material film between smooth surfaced rolls at a temperature under the melting point to obtain a thickness lower than the same, the transparency of the high density polyethylene is insufficiently improved by 35 only passing the film through a pair of rolls at the same temperature, as in the prior art, and that by using three heating rolls, heating from the outside, providing

the rolls with a temperature difference, and then rapidly cooling, a high density polyethylene can be obtained with a remarkably high transparency. It was learned that, according to the process, not only the roughness of the crystalline portions on the film--  
 5 surface, i.e., the external haze, but also the internal haze can be greatly reduced. Further, according to the present invention, and based on this discovery, there is provided a process for producing a high transparency  
 10 high density polyethylene film having a haze of less than 10% characterized by passing an original material film comprised of a high density polyethylene having a density of  $0.935 \text{ g/cm}^3$  or more through three heating rolls under the below mentioned temperature conditions  
 15 and then cooling the same. Note that, with regard to the temperature conditions of the above-mentioned heating rolls, designating the three rolls in the order of the passage of the original material film as the first heating roll (hereinafter referred to as " $R_1$ "),  
 20 the second heating roll (hereinafter referred to as " $R_2$ "), and the third heating roll (hereinafter referred to as " $R_3$ "), the temperature of  $R_2$  is set higher than the temperatures of  $R_1$  and  $R_3$  and the temperature of  $R_2$  is set at  $105^\circ\text{C}$  or more below the melting point  
 25 of the film. In particular, it is preferable to pass the original material film formed by inflation forming by a blow ratio of 3 or more under the above-mentioned temperature conditions for a draw ratio of 3 or more.

30 In the high density polyethylene type film of the first aspect of the present invention, an attempt is made to eliminate the above-mentioned problem points by the formation of a film of at least 50% by weight of high density polyethylene having a density of  $0.935 \text{ g/cm}^3$ , preferably 70% by weight or more, and a so-called high pressure low density polyethylene (herein-  
 35 after referred to as "LDPE") having a density of  $0.910$

g/cm<sup>3</sup> to 0.930 g/cm<sup>3</sup>.

Further, in the high density polyethylene type film of the second aspect, an attempt is made to eliminate the above-mentioned problem points by forming a film from a composition comprised of at least 50% by weight of a high density polyethylene having a density of 0.935 g/cm<sup>3</sup>, preferably 70% by weight or more, and a straight chain low density polyethylene copolymer (hereinafter referred to as "L-LDPE") having a density of 0.88 g/cm<sup>3</sup> to 0.930 g/cm<sup>3</sup>, then heat treating the same by three or more heating rolls having a superior surface gloss.

The high density polyethylene constituting the original material high density polyethylene film in the present invention may be an ethylene homopolymer or a copolymer of ethylene and one type or two types or more of comonomers. As an example of the copolymer involved, mention may be made of ethylene/propylene, ethylene/-butene-1, and ethylene/hexene-1 copolymers. Further, the high density polyethylene may be a blend with other polymers or may be a composition including antioxidants, dyes, inorganic fillers, and other additives. As examples of the other polymers to be blended therewith, mention may be made of low density polyethylene, polypropylene, copolymers of ethylene and vinyl acetate, and copolymers of ethylene and ethylene acrylate. At this time, the high density polyethylene is preferably included in an amount of at least 50%, preferably 70% or more.

The original material film is produced by the inflation process, T-die process, and various other film-forming processes. In particular, good results can be obtained by applying the process of production of the present invention to a high density polyethylene film produced by the inflation process, where transparency is a problem.

The density of the high density polyethylene is



0.935 g/cm<sup>3</sup> or more, preferably 0.935 to 0.975 g/cm<sup>3</sup>, more preferably 0.945 to 0.960 g/cm<sup>3</sup>. With a density of less than 0.935 g/cm<sup>3</sup>, it is impossible to provide superior properties to the HDPE film, e.g., nerve  
5 strength (Young's modulus), barrier property (moisture proofness), impact strength. When applying the present invention to a relatively high molecular weight polyethylene type resin or resin composition having the above density and seeking a greater strength in a film  
10 including at least 50% of a high density polyethylene, more preferably 70 to 90%, the melt index of the high density polyethylene (according to JIS K-7210, measurement under condition 4, hereinafter referred to as "MFR") should be made 1.0 g/10 min or less, preferably  
15 0.5 g/10 min or less, more preferably 0.1 g/10 min or less, particularly preferably 0.06 g/10 min or less. The original material film is formed by the inflation process.

The MFR of the LDPE and L-LDPE is usually 0.1 to  
20 10.0 g/10 min, preferably 0.1 to 3.0 g/10 min, particularly preferably 0.1 to 2.0 g/10 min. If an LDPE or L-LDPE with an MFR of less than 0.1 g is used, the fluidity is poor and thus the below mentioned formability of the film is poor, making production of an excellent  
25 film difficult. On the other hand, if an LDPE or L-LDPE with an MFR of over 10.0 g/10 min is used, a film having an excellent strength cannot be obtained.

The blow ratio in the inflation molding is preferably 3 or more. When less than 3, the orientation in  
30 the lateral direction is small and the heat treatment of subsequent processes will result in an overly large orientation in the longitudinal direction, making it difficult to obtain a film with a sufficiently high strength.

35 As the L-LDPE which can be used in the production of the film of the present invention, use may be made of one comprised of ethylene and  $\alpha$ -olefin. As the  $\alpha$ -olefin,

use is suitably made of one having 3 to 10 carbon atoms, for example, propylene, butene-1, hexene-1, octene, 4-methyl-pentene. Further, the L-LDPE used is one with a density of  $0.88 \text{ g/cm}^3$  to  $0.930 \text{ g/cm}^3$ . Production of a straight chain low density PE copolymer having a density of less than  $0.88 \text{ g/cm}^3$  is extremely difficult. Further, if the density of the straight chain low PE copolymer is over  $0.930 \text{ g/cm}^3$ , there is the inconvenience that the heat sealability cannot be improved.

The film of the present invention can be formed from the above-mentioned high density PE and L-LDPE, but of course, antioxidants, dyes, etc., may be added in accordance with need.

According to the film production process of the present invention, first, the above-mentioned high density PE or a composition comprised of L-LDPE or LDPE in the above-mentioned formulation proportion is formed into an original material film. As the method for forming the composition into a film, use may be made of the inflation process, T-die process, etc. When the above-mentioned composition is formed into a film by the inflation process, preferably the blow ratio is 3 or more. When the blow ratio is less than 3, the orientation in the lateral direction of the constituent molecules is insufficient and the orientation of the molecules in the longitudinal direction becomes too great due to the after-treatment accompanying the heat treatment, so there is the inconvenience that it is impossible to sufficiently improve the strength of the obtained film.

The "transparency" of the film in the present invention may be divided into the transparency of the film surface and interior. The transparency of HDPE film formed by the air-cooled inflation process (for example, one with a thickness of  $40 \text{ } \mu\text{m}$  [melt flow index (MI) =  $0.04 \text{ g/10 min}$ , density (D) =  $0.949 \text{ g/cm}^3$ ] was measured in terms of the surface factors and internal

factors, and as a result, a total haze of the film (hereinafter also referred to as simply the "haze") was, for example, 75%, which could be divided into a surface haze of 60% and an internal haze of 15%. In particular, the surface haze is derived from the scattering of-light due to the roughness of the fine structure caused by crystallization of the film surface layer. Physical smoothing of the surface is possible in the present invention by making the surface roughness of the film 0.1  $\mu$ m or less, whereby a remarkable improvement is achieved. The principle is the same, for example, as with making ground glass (translucent) transparent by applying cellophane tape to its two sides. As an example of application, there is known the method of applying to the two sides of an HDPE film a resin with a good transparency, or coextruding the same. However, as mentioned earlier, this method only reduces the scattering on the surface of the film, and with this alone, sufficient transparency cannot be obtained. Therefore, unless the internal haze is eliminated, it is impossible to obtain a film with a superior transparency of a haze of 15% or less in the above-mentioned case.

Therefore, the present inventors engaged in thoroughgoing research into the factors causing the internal haze and considered that the factors of the internal haze were the sum of the fluctuation in the orientation of the crystal lattice axes (birefringence of a, b, and c axes of polyethylene) and the fluctuation in the birefringence arising from the difference  $\Delta n$  of the birefringences of the amorphous layer (portion) and crystalline layer (portion). They found the orientation of the crystal lattice axes from the coefficient of orientation  $F_c$  and  $\Delta n$  from Lorenz-Lorentz's formula and studied the coefficient of transparency of the film from various data, and as a result, they discovered that  $F_c$  and  $\Delta n$  have a close relationship with the transparency

inside the film.

That is, the greater the  $F_c$  (the more uniform the  $c$  axis orientation) and the smaller the  $\Delta n$ , the better the transparency inside the film.

5 As a result, they discovered that, with a film thickness of 200  $\mu m$  or less, when  $F_c$  is 0.1 or more and  $\Delta n$  is 0.1070 or less, the transparency of an HDPE film with a smooth surface having a surface roughness of 0.1  $\mu m$  or less is remarkably improved, and thus completed  
10 the present invention.

Here, the coefficient of orientation of the  $c$  axis  $F_c$  is found by the Stein method from the polarization infrared spectrum (Macromolecule 1, 116, 1968):

$$F_a = (D730^{-1}) / (D730 + Z)$$

$$F_b = (D720^{-1}) / (D720 + Z)$$

$$F_a + F_b + F_c = 0$$

where,  $D730$  and  $D720$  are the infrared dichromatic ratios at 730  $cm^{-1}$  and 720  $cm^{-1}$  and

20  $F_a$ ,  $F_b$ , and  $F_c$  are the coefficients of orientation of the  $a$ ,  $b$ , and  $c$  axes of the crystals.

Further, the difference  $\Delta n$  of the birefringence of the crystal and amorphous portions is obtained from a modified Lorenz-Lorentz formula (Plastics, vol. 31, no. 2, p. 34)

$$\frac{\Delta n}{n} = \frac{(n^2 - 1) \times (n^2 + 2) \cdot \Delta \rho}{6n \cdot \rho}$$

where,  $nD$  is the birefringence of the film and is measured by an Atsube type birefringence meter,  $\rho$  is the film density and is found by a density gradient tube,  
30 and  $\Delta \rho$  is the difference in the density of the crystalline and amorphous portions. The values of the follow references were used.

Crystalline density: 1.01  $g/cm^3$ , E.R. Walter, J. Polymer Sci 21, 561<sup>c19</sup>

35 Amorphous density: 0.85  $g/cm^3$ , A.K. Doolittle: J. App. Phys. 22, 1471<sup>c19</sup>

The haze measurement was in accordance with ASTM D-1003.

Further, the surface roughness, which indicates the smoothness of the film surface, was measured in accordance with the test method of JIS B0601-55.

The resin in the present invention is designated as being a thermoplastic resin including at least 50% of HDPE having a density of  $0.935 \text{ g/cm}^3$  or more, preferably 70% or more, in that the superior characteristics of an HDPE film, e.g., nerve strength (Young's modulus), barrier property (moisture proofness), impact strength, etc., are available with a density of  $0.935 \text{ g/cm}^3$  and further in that these characteristics can be secured even when blending in various additives or molecular weight increasers to modify the resin or blending resins, by including at least 70% of the above-mentioned HDPE.

Further, in the present invention, the film surface roughness is made  $0.1 \text{ } \mu\text{m}$  or less because there is great external roughness in the case of HDPE, which scatters light at the surface, and this is a factor behind the greater external haze. This is one of the conditions for elimination of this roughness and creation of the highly transparent film desired in the present invention.

For the heating rolls, for example, use is made of metal rolls having a hard chrome plating on the surfaces thereof. These may be polished.

Further, it is possible to use rolls having smooth surfaces which are worked or finished to a mirror-like gloss.

Among the heating rolls, the temperature of the second roll ( $R_2$ ) must be made higher than that of the first roll ( $R_1$ ) and third roll ( $R_3$ ). That is, the original material film should be passed through heating rolls comprised of a system of  $R_1$ ,  $R_2$ , and  $R_3$  with the intermediate roll set to the highest temperature and a temperature difference given among the rolls.

The temperature of  $R_1$  is preferably  $50^\circ\text{C}$  or more,

55°C being particularly preferable.

The temperature of the above-mentioned  $R_2$  must be 105°C or more below the melting point of the original material film. Therefore, the heating rolls are all set  
5 to below the melting point of the original material film, but it is necessary to provide a temperature difference between  $R_2$  and the other rolls, i.e.,  $R_1$  and  $R_3$ . The temperature of  $R_1$  and  $R_3$  should be set to a temperature not higher than the temperature  
10 of  $R_2$ .

The temperature of  $R_3$  is preferably 70°C or more, 75°C or more being particularly preferable. If the temperature of  $R_3$  is over 120°C, an excellent transparency is difficult to obtain. Further, at less than  
15 70°C, the film will adhere to  $R_2$  and a sufficient transparency would be difficult to obtain.

In a preferred embodiment of the present invention,  $R_2$  is heated externally by an infrared heater, etc. The heating temperature is a temperature higher than  
20 80°C, but a temperature lower than the temperature at which the high density polyethylene would melt. Therefore, 180°C or less (suitably 160°C or less) is preferable. The heating enables the acquisition of a film having sufficient uniform transparency even with an  
25 original material thinner than 50  $\mu\text{m}$  and a draw ratio of 1 to 3. By way of reference, if the original material film is thinner than 50  $\mu\text{m}$ , a film having a uniform transparency cannot be obtained without external heating. At this time, the heating is preferably applied uniformly  
30 to the surface which comes in contact with the roll in a manner such that the above-mentioned temperature range is achieved.

The original material film may be passed through the clearance of the above-mentioned three heating  
35 rolls, which is less than the thickness of the original material film, to obtain a transparent film having a thickness less than that of the original material film.

The draw ratio is made 3 or less. If drawing is greater than 3, the orientation in the longitudinal direction would progress too far and a film with a sufficient high strength could not be obtained. The preferable draw ratio or compression ratio is larger than 1 and no more than 3.

The film which has passed through the heating rolls is then cooled. For example, it is cooled by two chill rolls (hereinafter referred to as  $R_4$  and  $R_5$ ). The temperature of the chill rolls is not particularly critical, but is preferably not more than  $70^\circ\text{C}$  and not less than  $30^\circ\text{C}$ . If over  $70^\circ\text{C}$ , the chill rolls would not be able to perform their function. If less than  $30^\circ\text{C}$ , it would be difficult to secure a sufficient flatness of the film.

The thickness of the original material film used in the present invention is not particularly limited and is decided by the desired thickness of the product, etc. This is thicker than the thickness of the finished film, but less than 3 times the film thickness, preferably 2.3 times or less, more preferably 1.05 to 1.8 times the film thickness.

According to the present invention, a highly transparent high density polyethylene having a haze less than 10% is obtained. The haze is measured according to ASTM D-1003. The haze in the present invention refers to the sum of the external haze and the internal haze.

The high density polyethylene film crystallizes at the surface in the free surface state after film formation by the inflation process, and lamella aggregates ( $\lambda = 100$  to  $110 \text{ \AA}$ ) protrude as roughness from the surface. The magnitude of the same corresponds to the wavelength ( $4000$  to  $8000 \text{ \AA}$ ) of visible light, so scattering occurs and the film becomes nontransparent.

Due to the transparency treatment of the present invention, the surface roughness is smoothed in a state of easy movement of molecular chains, the wavelength of

the roughness is 4000 Å or less, and the external haze is made excellent. The present invention has the important feature of enabling a reduction of not only the external haze, but also the internal haze. As factors of nontransparency from inside films, there are considered the nonuniform thickness of microcrystals and the internal voids included in the crystals.

In the present invention, due to the transparency treatment, for example, a density of of a film before treatment of 0.948 g/cm<sup>3</sup> is raised to a density of a film after treatment of 0.952 g/cm<sup>3</sup>, and it is considered that the above-mentioned internal voids and nonuniform layer are eliminated.

#### Examples

The present invention will now be explained by the following Examples and Comparative Examples.

#### Examples 1 to 3 and Comparative Examples 1 to 4

In the Examples and Comparative Examples, HDPE (D = 0.949 g/cm<sup>3</sup>, MI = 0.04 g/10 min) was subjected to the inflation process to produce an original material film 50 μm in thickness. The original material film was passed through heating rolls having a surface gloss (temperature below melting point of resin) to produce a film with a surface roughness of 0.1 μm or less and different Fc's and Δn's. The physical properties of the films are shown in Table 1.

However, in Example 3 and Comparative Example 4, use was made of a blend of HDPE and low density polyethylene (LDPE, D = 0.921, MI = 1.5). Otherwise, the procedures were the same as above.

- 1) Forming material: 65φ Ext, die: 100φ spiral
- 2) Temperature  $C_1 = C_2 = C_3 = H = D = 190^{\circ}\text{C}$
- 3) Take up speed: 15 m/min
- 4) Blow ratio (BVR) = 4.0
- 5) Film thickness: 50 μm



Table 1

	Example				Comparative Example			
	1	2	3	4	1	2	3	4
Resin used	HDPE	HDPE	HDPE (80%) LDPE (20%)	HDPE (80%) L-LDPE (20%)	HDPE	HDPE	HDPE	HDPE (60%) LDPE (40%)
Fc	0.201	0.315	0.150	0.160	0.023	0.023	0.195	0.050
$\Delta n$	0.1057	0.1048	0.1035	0.1040	0.1075	0.1063	0.1077	0.1060
<u>Film properties</u>								
Haze (%)	9.5	3.5	4.2	-3.8	28	23	19	15
Impact (kg·cm/mm)	280	250	20	285	260	290	250	180
Young's modulus	9,800	10,500	7,200	7,800	8,800	8,500	8,300	5,500
Roughness ( $\mu m$ )	0.108	0.075	0.090	0.085	-	0.205	-	0.175
(Film thickness 45 $\mu m$ )								

L-LDPE = density 0.917 g/cm<sup>3</sup>, MFR = 0.79 g/10 min, ethyl groups/100C = 20 ethylene-butene-1 copolymer.

Example 4

Use was made of an HDPE having a melt index of 0.05 g/10 min and a density of 0.949 g/cm<sup>3</sup>. Using the inflation process, a blow ratio of 5, a frost line of 500 mm, and a take up speed of 10 m/min, a 100 μm thick original material film was formed. This was drawn at a draw ratio of 3 and heat treated under the conditions shown in Table 1. Note that the chill roll temperatures were  $R_4 = R_5 : 50^{\circ}\text{C}$ .

10 Note that in the following examples, the breaking strength was determined according to JIS-Z-1702.

Examples 5 to 9 and Comparative Examples 5 to 7

High density polyethylene film was obtained in the same manner except for using the conditions shown in 15 Table 2. The results are shown in Table 2.

Comparative Example 8

High density polyethylene film was obtained in the same manner as in Example 2, except that the blow ratio was made 2 and the conditions shown in Table 2 were 20 used.

The results are shown in Table 2.

Table 2

	R <sub>1</sub> (°C)	R <sub>2</sub> (°C)	R <sub>3</sub> (°C)	Haze (%)	Breaking strength (kg/cm <sup>2</sup> ) MD/TD	Thickness after treatment (μm)
Ex. 4	70	128	85	5.5	445/415	82
5	105	128	105	5.2	475/398	67
6	105	120	105	5.6	460/408	73
7	60	120	85	8.8	453/438	87
8	110	120	85	7.1	488/385	68
9	70	121	85	7.3	461/418	84
Com. Ex. 5	70	138	85	Stuck on 2nd roll		
6	70	125	130	58	453/395	72
7	70	90	85	68	473/435	68
8	70	125	105	6.3	553/223	65

Examples 10 to 12

High density polyethylene (density 0.950 g/cm<sup>3</sup>, blow ratio 3) with an MFR of 0.05 g/10 min and a melting point of 130°C was subjected to a usual inflation process to produce original materials having thicknesses of 20 μm, 30 μm, and 40 μm (hereinafter referred to as "original material (1)", "original material (2)", and "original material (3)"). These original materials (shown in Table 3) were used to produce films with thicknesses as shown in Table 4, using rolls with a superior surface gloss at an R<sub>1</sub> temperature of 85°C, an R<sub>2</sub> temperature of 115°C, an R<sub>3</sub> temperature of 110°C, and a chill roll R<sub>4</sub> and R<sub>5</sub> temperature of 50°C. The haze of the obtained films was measured, and the results are shown in Table 3. Note that R<sub>2</sub> was heated by an infrared heater.

Table 3

Example	Orig. mat. type	Film Thickness (μm)	Haze value (%)
Ex. 10	Orig. mat. (1)	15	2.5
" 11	" (2)	21	2.8
" 12	" (3)	50	4.5
Com. Ex. 9	" (1)	15	-
" 10	" (2)	21	-
" 11	" (3)	30	-

Note that the films obtained by Examples 10 to 12 were all uniformly transparent. Note further that Comparative Examples 9 to 11 did not make use of an infrared heater, but used heating rolls for the heating.

In Comparative Examples 9 to 11, films having a uniform transparency could not be obtained.

Examples 13 to 14 and Comparative Examples 12 to 14

For the high density PE, use was made of one having  
5 a density of  $0.950 \text{ g/cm}^3$  and a melt index of  $0.04 \text{ g/10 min.}$  For the straight chain low density PE copolymer, use was made of one with a density of  $0.88 \text{ g/cm}^3$  and a melt index of  $4 \text{ g/10 min.}$

The formulation ratio of high density PE and  
10 straight chain low density PE copolymer was 100/0 in Comparative Example 12, 95/5 in Comparative Example 13, 70/30 in Example 13, 60/40 in Example 14, and 40/60 in Comparative Example 14.

The compositions comprised of the above formulations  
15 were subjected to the inflation process to make films having thicknesses of  $100 \text{ }\mu\text{m}$ , which were used as the original material films. At this time, the forming temperature was  $200^\circ\text{C}$  and the blow ratio 3.

The original material films produced as above were  
20 heat treated by the three heating rolls, and were then cooled by the two chill rolls to obtain films  $70 \text{ }\mu\text{m}$  in thickness. The temperatures of the heating rolls were set to  $100^\circ\text{C}$  for the first roll ( $R_1$ ),  $115^\circ\text{C}$  for the second roll ( $R_2$ ), and  $100^\circ\text{C}$  for the third roll ( $R_3$ ).  
25 Further, the temperature of the chill rolls was set to  $30^\circ\text{C}$ .

The physical properties of the films thus obtained are shown in Table 4.

Table 4

		Haze value (%)	Yield strength (kg/cm <sup>2</sup> )	Young's modulus (kg/cm <sup>2</sup> )	Low temp. sealability (°C)	Impact strength (kg·cm/mm)
Com. Ex. 12	6	2	10,500	135	188	
"	13	6.0	1.9	9,300	133	210
Ex.	13	4.3	1.75	8,700	120	320
"	14	4.5	1.35	7,600	115	315
Com. Ex. 14	4.8	0.98	5,100	105	285	

The physical properties were determined by the following methods:

Haze ... according to ASTM D1003

Yield strength ... according to JIS Z1702

Young's modulus ... according to ASTM D882

Heat sealability ... First, the film was cut into narrow strips 15 mm wide. These were heat sealed under conditions of a sealing pressure of 2 kg/cm<sup>2</sup> and a sealing time of 1 second, with different temperatures, then the test pieces were peeled at a speed of 300 mm/min to determine the peeling strength. The heat sealability was expressed by the sealing temperature of test pieces displaying a peeling strength of 1 kg.

Impact strength ... according to ASTM-D-781

From the results of Table 4, it was confirmed that the film of the present invention had superior impact strength and a good balance of such physical properties as the heat sealability, haze, yield strength, and Young's modulus.

#### EFFECTS OF THE INVENTION

According to the present invention, as indicated also by the above-mentioned embodiments, a high density

polyethylene type film with a small haze and superior transparency is obtained. This film further has both transparency and film strength, so although conventional high density polyethylene films were considered difficult to make highly transparent without obstructing the film strength, this was realized in the present invention. Therefore, the industrial significance is great. The high density polyethylene type film of the present invention, having the constitution explained above, has flexibility and a suitable melting temperature, so in addition to the superior characteristics of high density polyethylene, i.e., high strength and high transparency, it is provided with an excellent impact resistance and heat sealability. Therefore, the film of the first aspect of the invention can be easily heat sealed at a low temperature and is difficult to break even under impact. Further, according to the process of production of the present invention, it is possible to produce a film having not only a high strength, easy heat sealability, and high impact strength, but also an excellent transparency.

CLAIMS

1. A film having a thickness of 10 to 200  $\mu\text{m}$  comprised of high density polyethylene having a density of 0.935  $\text{g/cm}^3$  or more, said high density polyethylene type film having a film surface roughness of 0.001 to 0.15  $\mu\text{m}$ , a coefficient of C axis orientation of the crystals in the film ( $F_c$ ) of 0.10 to 0.50, a difference  $\Delta n$  of the birefringence of the amorphous portions and crystalline portions in the film of 0.1000 to 0.1070, and a transparency of a haze of less than 10%.

2. A process for producing a high transparency high density polyethylene film having a haze of less than 10% comprised of the steps of passing an original material film, formed using high density polyethylene having a density of 0.935  $\text{g/cm}^3$  or more by inflation at a blow ratio of 3 or more, through at least three heating rolls under the below mentioned temperature conditions, heat treating the same under a draw ratio of 5 or less, and then cooling the same, said process for producing a high density polyethylene film being characterized in that, as to the temperature conditions of the above-mentioned heating rolls, designating the heating rolls in the order of the passage of said original material film as the first, or third from the last, heating roll (hereinafter referred to as " $R_1$ "), the second from the last heating roll (hereinafter referred to as " $R_2$ "), and the last heating roll (hereinafter referred to as " $R_3$ "), the temperature of  $R_2$  is set higher than the temperatures of  $R_1$  and  $R_3$  and the temperature of  $R_2$  is set at 105°C or more below the melting point of said film.

3. A process for production according to claim 2, wherein use is made, in addition to the heating rolls, of heating by an external heating means.

4. A film having a thickness of 10 to 200  $\mu\text{m}$  comprised of 50% by weight or more of high density polyethylene having a density of 0.935  $\text{g/cm}^3$  or more



and high pressure low density polyethylene having a density of 0.910 to 0.930 g/cm<sup>3</sup>, said high density polyethylene type film having a film surface roughness of 0.001 to 0.17  $\mu$ m, a coefficient of C axis orientation of the crystals in the film (Fc) of -0.3 to +0.50, a difference  $\Delta n$  of the birefringence of the amorphous portions and crystalline portions in the film of 0.1000 to 0.1070, and a transparency of a haze of less than 10%.

5. A film having a thickness of 10 to 200  $\mu$ m comprised of 50% by weight or more of high density polyethylene having a density of 0.935 g/cm<sup>3</sup> or more and straight chain low density polyethylene having a density of 0.880 to 0.930 g/cm<sup>3</sup>, said high density polyethylene type film having a film surface roughness of 0.001 to 0.17  $\mu$ m, a coefficient of C axis orientation of the crystals in the film (Fc) of -0.3 to +0.50, a difference  $\Delta n$  of the birefringence of the amorphous portions and crystalline portions in the film of 0.1000 to 0.1070, and a transparency of a haze of less than 10%.

## INTERNATIONAL SEARCH REPORT

0246328

International Application No.

PCT/JP86/00566

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl <sup>4</sup> B29C71/02, B29D7/01, B29C55/18, B29C55/06, B29C55/28, C08J7/00, C08J5/18		
II. FIELDS SEARCHED		
Minimum Documentation Searched*		
Classification System	Classification Symbols	
IPC	B29C71/02, B29D7/01, B29C55/06, B29C55/18, B29C55/28, C08J5/18, C08J7/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched*		
Jitsuyo Shinan Koho		1952 - 1986
Kokai Jitsuyo Shinan Koho		1971 - 1986
III. DOCUMENTS CONSIDERED TO BE RELEVANT**		
Category	Citation of Document, with indication where appropriate, of the relevant passages	Relevant to Claim No. 1*
A	JP, A, 53-117069 (Sumitomo Chemical Co., Ltd.) 13 October 1978 (13. 10. 78) (Family: none)	2-3
A	JP, A, 51-16360 (Nippon Petrochemicals Co., Ltd.) 9 February 1976 (09. 02. 76) & GB, A, 1478576 & FR, A, 2282985 & DE, A, 2534302	2-3
A	JP, A, 53-31768 (Nippon Petrochemicals Co., Ltd.) 25 March 1978 (25. 03. 78) (Family: none)	2-3
A	JP, A, 59-5032 (B.P. Chemicals Limited) 11 January 1984 (11. 01. 84) (Family: none)	2-3
<p>* Special categories of cited documents: 13</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
January 28, 1987 (28. 01. 87)		February 9, 1987 (09. 02. 87)
International Searching Authority		Signature of Authorized Officer
Japanese Patent Office		

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